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(54) Title: IONIC CATALYST FOR THE PRODUCTION OF POLY- α -OLEFINS OF CONTROLLED TACTICITY			
(57) Abstract			
An ionic catalytic process for the production of poly- α -olefin resins of stereochemical configuration, which process permits improved control over tacticity, molecular weight and molecular weight distribution. Such poly- α -olefins are produced to the desired tactic configurations by polymerization of α -olefin monomers in the presence of a catalyst system comprising an ionic reaction product of a cyclopentadienyl Group 4 metal compound (a "metallocene") of specific structure and an activator compound comprising a cation capable of irreversibly reacting with at least one non-cyclopentadienyl ligand of the metallocene and an anion which is compatible with and non-coordinating to the metallocene cation generated upon reaction of the metallocene with said activator compound. By appropriate selection of the metallocene and activator components, the catalyst system can be tailored for the production of polymers having stereochemical configuration.			

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APPLICATION FOR PATENT

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10 Title: IONIC CATALYST FOR THE PRODUCTION OF
POLY- α -OLEFINS OF CONTROLLED TACTICITY

SPECIFICATION

15

FIELD OF THE INVENTION

This invention relates to an ionic catalytic process for the production of poly- α -olefin resins which process permits improved control over tacticity, 20 molecular weight and molecular weight distribution. Such poly- α -olefins are produced to the desired tactic configurations by polymerization of α -olefin monomers in the presence of a catalyst system comprising an ionic reaction product of a cyclopentadienyl Group 4 metal compound (hereafter a "metallocene") of specific structure and an activator compound comprising a 25 cation which is capable of reacting with a non-cyclopentadienyl ligand of the metallocene and an anion which is compatible with and non-coordinating to the metallocene cation generated upon reaction of the metallocene with said activator compound. By appropriate selection of the metallocene and activator components, the catalyst system can be tailored to the production of 30 the desired weight average molecular weight (M_w) poly- α -olefins with end group functionalization and select tacticity type and level such as isotactic, syndiotactic or hemiisotactic configurations.

BACKGROUND OF THE INVENTION

35 Polymers comprised of α -olefin monomers have hydrocarbyl groups pendent from the polymer backbone chain. Relative to the polymer backbone chain, the pendent hydrocarbyl groups may be arranged in different stereochemical configurations which are denominated as atactic, isotactic, or syndiotactic pendent group configuration.

40 The degree and type of tacticity of a polyolefin molecule is a critical determinant of the physical properties which a resin composed of such polymer molecules will exhibit. Other critical determinants of the properties

which a resin will exhibit are the type and relative concentration of monomers and comonomers, the weight average molecular weight (M_w) of the polymer molecules comprising the resin bulk, the molecular weight distribution (MWD) and the composition distribution of the resin.

5 Important from a commercial standpoint is the rate or productivity at which a catalyst system will produce a poly- α -olefin resin of a desired set of properties in terms of tacticity, weight average molecular weight and molecular weight distribution.

10 The weight average molecular weight (M_w) of a poly- α -olefin is an important physical property determinant of the practical uses to which such polymer can be put. For end use applications which require high strength and low creep, the M_w of such a resin must generally be in excess of 100,000. Further, for such high strength applications, the poly- α -olefin resin must generally have a high degree of crystallinity. The degree of crystallinity 15 which a poly- α -olefin is capable of obtaining is, in major part, determined by the stereochemical regularity of the hydrocarbyl groups which are pendent to the polymer molecule backbone, i.e., the tacticity of the polymer.

20 Five types of tacticity have been described in poly- α -olefins: atactic, normal isotactic, isotactic stereoblock, syndiotactic, and hemiisotactic. Although all of these tacticity configurations have been primarily demonstrated in the case of polypropylene, in theory each is equally possible 25 for polymer comprised of any α -olefin, cyclic olefin or internal olefin.

25 For any of the above described tacticity materials the final resin properties and its suitability for particular applications depend on the type of tacticity, (stereoregularity) the melting point, the average molecular weight, the molecular weight distribution, the type and level of monomer and comonomer, the sequence distribution, and the presence or absence of head or end group functionality. Accordingly, the catalyst system by which such a stereoregular poly- α -olefin resin is to be produced should, desirably, be 30 versatile in terms of M_w , MWD, tacticity type and level, and comonomer choice. Further, the catalyst system should be capable of producing these polymers with or without head and/or end group functionality, such as olefinic unsaturation. Still further, such catalyst system must be capable, as a 35 commercially practical constraint, of producing such resins at an acceptable production rate. Most preferably, the catalyst system should be one which, at its productivity rate, provides a resin product which does not require a

subsequent treatment to remove catalyst residue to a level which is acceptable for the resin in the end use application desired. Finally, an important feature of a commercial catalyst system is its adaptability to a variety of processes and conditions.

5 Conventional titanium based Ziegler-Natta catalysts for the preparation of isotactic polymers are well known in the art. These commercial catalysts are well suited for the production of highly crystalline, high molecular weight materials. The systems are, however, limited in terms of molecular weight, molecular weight distribution, and tacticity control. The
10 fact that the conventional catalysts contain several types of active sites further limits their ability to control the composition distribution in copolymerization.

15 Catalysts that produce isotactic polyolefins are also disclosed in U.S. Patent No. 4,794,096. U.S. '096 discloses a chiral, stereorigid metallocene catalyst which is activated by an alumoxane cocatalyst which is reported to polymerize olefins to isotactic polyolefin forms. Alumoxane cocatalyzed metallocene structures which have been reported to polymerize stereoregularly are the ethylene-bridged bis(tetrahydroindenyl) titanium and -zirconium (IV) catalyst. Wild et al., in J. Organomet. Chem. 232, 233-47
20 (1982), and later Ewen and Kaminsky et al., reported to polymerize α -olefins stereoregularly. Further reported in West German Off DE 3443087A1, (1986), but without giving experimental verification, is that the bridge length of such stereorigid metallocenes can vary from a C₁ to C₄ hydrocarbon and the metallocene rings can be simple or bicyclic but must be asymmetric.

25 Metallocene-alumoxane catalyst generally require a high content of alumoxane cocatalyst to be sufficiently productive for commercial use. Accordingly, metallocene-alumoxane produced isotactic poly- α -olefin resins generally have a higher than desired catalyst residue content. Hafnium systems, which yield polymers of higher average M_w than the zirconium analogues, have very low activities even at high alumoxane concentrations.

30 Syndiotactic polyolefins were first disclosed by Natta et al. in U.S. Patent No. 3,258,455. As reported, Natta obtained syndiotactic polypropylene by using a catalyst prepared from titanium trichloride and diethyl aluminum monochloride. A later patent to Natta et al., U.S. Patent
35 No. 3,305,538, discloses the use of vanadium triacetylacetone or

halogenated vanadium compounds in combinations with organic aluminum compounds for production of syndiotactic polypropylene.

More recently a new method of producing isotactic polymers from an alumoxane cocatalyzed, or activated, metallocene which in its natural state has chirality centered at the transition metal of the metallocene, was reported by Ewen, J.A., in J. Amer. Chem. Soc., 106, 6355, (1984) and Kaminsky, W., et al., in Angew. Chem. Int. Ed. Eng., 24, 507-8 (1985).

U.S. Patent No. 4,892,851 describes catalyst systems consisting of a bridged metallocene having at least two differently substituted cyclopentadienyl ring ligands which, when cocatalyzed with an alumoxane, is stated to be capable of production of syndiotactic polypropylene. Again, in commercial production to obtain a sufficient productivity level with such catalyst system, the content of alumoxane is undesirably high and consequently the catalyst residue in the resin so produced is undesirable.

In all methylalumoxane/metallocene catalyst systems the polymer characteristics (M_w , MWD, tacticity type, comonomer incorporation, etc.) are controlled either by modifications to the structure of the metallocene precursor or by adjustment of the process conditions (temperature, pressure, concentrations). In general, adjustment of process conditions does not allow independent control of tacticity level, M_w and comonomer content. Addition of chain transfer agents such as hydrogen gas to the reactor gives lower molecular weight products without affecting tacticity, however, the resulting polymer no longer has unsaturated end groups. End group functionalization is often an important feature in the application of low molecular weight polymers. Given these limitations, one must prepare a wide variety of differently substituted metallocene precursors to access the entire range of desired materials.

Ionomically activated catalyst systems are becoming more desirable to minimize or avoid difficulties encountered with alumoxane activated systems. The first of various publications regarding ionic activators was by Turner et al. in EPA 277,004 and EPA 277,003. EPA 277,004 and 277,003 describe bis-cyclopentadienyl metallocene catalysts for the production of homo- or copolymers of polyolefins, including polypropylene.

PCT application WO 92/05208 describes bis-cyclopentadienyl, ionically activated moieties useful for the production of syndiotactic polypropylene. Dow Corporation has several publications which describe

mono-cyclopentadienyl, ionically activated moieties useful for the production of polyolefins, however the teachings of the publications are to polyethylene, not stereoregular polypropylene or polymers having stereoregular characteristics.

5 In view of the difficulty and practical limitations in the synthesis of bridged bis(cyclopentadienyl) metallocene complexes necessary for the production of an alumoxane-activated or ionically activated metallocene catalyst system capable of producing crystalline poly- α -olefins, it would be desirable to develop new methods of activation which expand the product 10 capability of a particular metallocene catalyst.

SUMMARY OF THE INVENTION

15 The invention comprises a highly versatile process and catalyst system for the production of stereoregular polyolefins, particularly useful for the production of controlled tacticity poly- α -olefins with variable molecular weight, molecular weight distribution, stereoregularity and end group functionalization. The process comprises contacting α -olefin monomer and comonomers in a suitable solvent at a temperature of from about -10° C to about 300° C with an ionic catalyst to produce a polymer.

20 The ionic catalyst comprises a cationic cyclopentadienyl derivative of the Group 4 metals, said derivatives containing at least one cyclopentadienyl (Cp) ligand, electrochemically balanced by one or more non-coordinating anions.

25 In accordance with this invention, when the cyclopentadienyl Group 4 metal component (hereafter referred to as a "metallocene") selected for the ionic catalyst is a chiral racemic compound, there may be produced a poly- α -olefin which is predominantly of an isotactic stereochemical configuration. In accordance with this invention, when the metallocene selected for the 30 ionic catalyst is a bridged stereorigid compound composed of one Cp ligand and a heteroatom ligand, there may also be produced a poly- α -olefin which is predominantly of the syndiotactic stereochemical configuration. In general the ionic catalyst system of this invention derived from a particular metallocene complex will produce a polymer having the same type of tacticity which would be produced using methylalumoxane as the activating reagent.

35 The ionic catalyst system allows new levels of control of the polymer properties (M_w , MWD, tacticity level, end groups, comonomer content, etc.)

- 6 -

for a single metallocene precursor by use of various non-coordinating anions as well as by the addition of third components such as Lewis bases and chiral Lewis bases. It has been discovered that the structure of the non-coordinating anion in the ionic catalyst species has a dramatic effect on the 5 activity, molecular weight, comonomer incorporation, and end group unsaturation. This tendency coupled with the wide variety of suitable non-coordinating anions available allow a single metallocene catalyst precursor to be converted into a variety of chemically different active catalysts which produce polymers having different densities (in copolymerizations), 10 molecular weights, and chain end structures under identical reactor conditions. This versatility is important in the use of metallocene catalysts to produce a broad family of polyolefins (e.g., PE, LLDPE, EP, PP etc.) but it is particularly important for the production of tacticity controlled poly- α -olefins (e.g., syndiotactic, isotactic) because 1) the preparation of new bridged 15 metallocene structures is synthetically difficult 2) adjusting process parameters such as temperature or monomer concentration to adjust the molecular weight of the product also affects the level of tacticity and the melting point, and 3) use of chain transfer agents such as H₂ to lower the molecular weight causes loss of end-group unsaturation which is a desirable 20 and unique feature of poly- α -olefins produced using metallocene-based catalysts.

Advantages of employing monocyclopentadienyl-heteroatom metallocene catalyst activated by ionic systems include: (1) greater ability than bis (cyclopentadienyl) metallocenes to incorporation larger aliphatic olefins; 25 (2) the ability to produce high molecular weight polymers, especially when using Ti based metallocenes.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

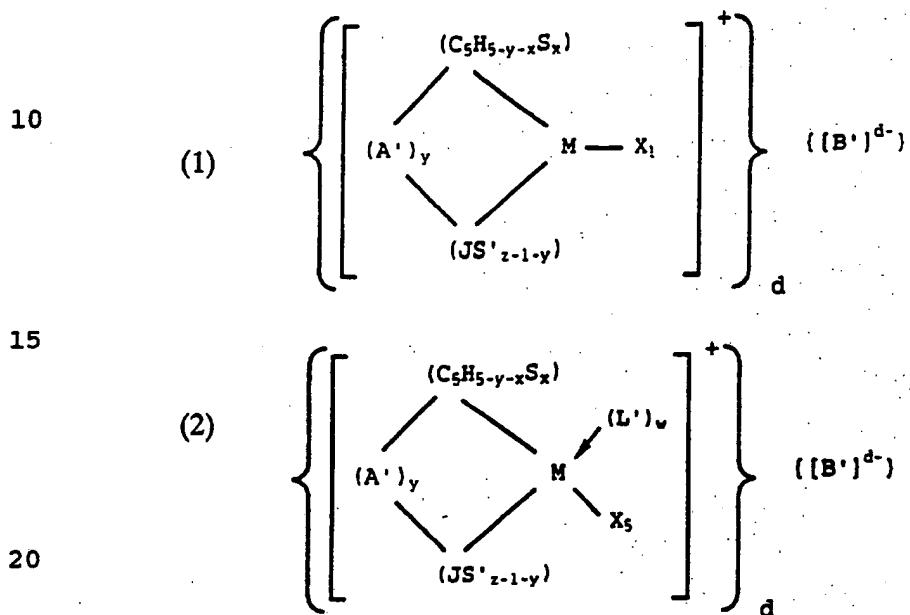
The invention provides a method for producing a poly- α -olefin of a 30 desired stereochemical configuration. The poly- α -olefin polymers may be produced to a weight average molecular weight (M_w) which suits it to high strength applications, and the so produced resin contains minimal catalyst residue which does not require deashing of the resin to render it suitable for desired end use applications.

- 7 -

Ionic Catalyst System - General Description

The process of this invention is practiced with that class of ionic catalyst referred to, disclosed, and described in PCT International Application WO 92/00333.

5 The ionic catalysts used in this invention to produce stereoregular poly- α -olefins can be represented by one of the following general formulae:



wherein:

(C₅H_{5-y-x}S_x) is a cyclopentadienyl ring substituted with from zero to five S radicals;

25 x is from 1 to 5 denoting the degree of substitution;

M is titanium, zirconium or hafnium;

L' is a neutral Lewis base;

A' is a bridging group, which group may serve to restrict rotation of the Cp and Cp* rings;

30 X₁ is a hydride radical, hydrocarbyl radical, substituted-hydrocarbyl radical, hydrocarbyl-substituted organometalloid radical or halocarbyl-substituted organometalloid radical;

X₅ is a hydride radical, hydrocarbyl radical or substituted-hydrocarbyl radical, halocarbyl radical or substituted halocarbyl radical, hydrocarbyl-substituted organometalloid radical or halocarbyl-substituted

organometalloid radical, which radical may optionally be covalently bonded to both M and L';

(JS'_{z-1-y}) is a heteroatom ligand in which J is an element from Group 15 of the Periodic Table of Elements with a coordination number of 3 or an element from Group 16 with a coordination number of 2; S' is a radical group which is a hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, hydrocarbyl-substituted organometalloid, or halocarbyl-substituted organometalloid; and z is the coordination number of the element J;

10 y is 0 or 1;

w is an integer from 0 to 3;

B' is a chemically stable, non-nucleophilic anionic complex preferably having a molecular diameter about or greater than 4 angstroms; and

15 d is an integer representing the charge of B'.

The improved catalysts are preferably prepared by combining at least two components. The first component is a cyclopentadienyl derivative of a Group 4 metal compound containing at least one ligand which will combine with the second component or at least a portion thereof such as a cation portion thereof. The second component is an ion-exchange compound comprising a cation which will irreversibly react with at least one ligand contained in said Group 4 metal compound (first component) and a non-coordinating anion which is either a single coordination complex comprising a plurality of lipophilic radicals covalently coordinated to and shielding a central formally charge-bearing metal or metalloid atom or an anion comprising a plurality of boron atoms such as polyhedral boranes, carboranes and metallacarboranes.

30 The cation portion of the second component may comprise Bronsted acids such as protons or protonated Lewis bases or may comprise reducible Lewis acids such as ferricinium, troplium, triphenylcarbenium or silver cations.

35 In general, suitable anions for the second component may be any stable and bulky anionic complex having the following attributes: 1) the anion should have a molecular diameter greater than 4 angstroms; 2) the anion should form stable ammonium salts; 3) the negative charge on the anion should be delocalized over the framework of the anion or be localized

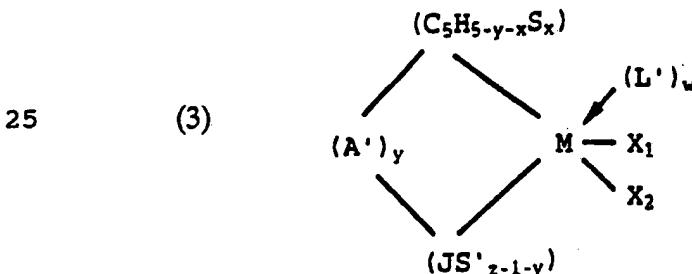
- 9 -

within the core of the anion; 4) the anion should be a relatively poor nucleophile; and 5) the anion should not be a powerful reducing or oxidizing agent. Anions meeting these criterias - such as polynuclear boranes, carboranes, metallacarboranes, polyoxoanions and anionic coordination complexes are well described in the chemical literature. Upon combination of the first and second components, the cation of the second component reacts with one of the ligands of the first component, thereby generating an anion pair consisting of a Group 4 metal cation and the aforementioned anion, which anion is compatible with and noncoordinating towards the Group 4 metal cation formed from the first component. The anion of the second compound must be capable of stabilizing the Group 4 metal cation without interfering with the Group 4 metal cation's ability to function as a catalyst and must be sufficiently labile to permit displacement by an olefin, diolefin or an acetylenically unsaturated monomer during polymerization.

15

A. The Metallocene Component

The Group 4 metal compounds; i.e., titanium zirconium and hafnium metallocene compounds, useful as first compounds in the preparation of the improved catalyst of this invention are cyclopentadienyl derivatives of titanium, zirconium and hafnium. In general, useful complexes may be represented by the following general formula:



30 wherein:

35 X_1 and X_2 are, independently, hydride radicals, hydrocarbyl radical, substituted hydrocarbyl radical, halocarbyl radicals, substituted halocarbyl radicals, and hydrocarbyl - and halocarbyl -substituted organometalloid radicals, or are joined and bound to the metal atom to form a metallacycle ring containing from about 3 to about 20 carbon atoms; in addition, if $y=0$, then $w>0$; and all other symbols are as described above.

- 10 -

The Group 4 metal compounds useful as the first component in ionic catalyst system for the production of crystalline poly- α -olefins are cyclopentadienyl derivatives of titanium, zirconium or hafnium which compounds are either chiral racemic compounds, or are non-chiral bridged 5 stereorigid compounds composed of two differently substituted ligands. Such metallocene compounds are represented by the general formula set forth in equation 1-3, wherein M, X₁, X₂ and L are defined as in Equations 1-2 and (1) A' is a divalent hydrocarbyl or silahydrocarbyl radical which structurally bridges together the cyclopentadienyl ring and the J ligand group to impart 10 stereorigidity to the Group 4 metal compound such that the Group 4 metal compound is a chiral compound either in its pure L or pure D optical isomer form or a racemic mixture thereof; or (2) A' is a divalent hydrocarbyl or silahydrocarbon radical which structurally bridges ligands having distinctly different chemical structures.

15

Stereorigid Chiral Metallocene Components for Poly- α -Olefins of Enhanced Tacticity

Preferable metallocene precursors for producing poly- α -olefins having enhanced isotactic character are those where S and S' are chosen such that 20 the metallocene framework has no plane of symmetry containing the metal center.

Preferable metallocene precursors for the production of poly- α -olefins having enhanced syndiotactic character are also those where S and S' are chosen such that the ligands are coordinated with the transition metal and 25 have substantially different steric bulk. In order to produce a syndiotactic polymer the pattern of the groups substituted on the Cp-ring is important. Thus, by "steric difference" or "sterically different" as used herein, it is intended to imply a difference between the steric characteristics of the Cp ring and heteroatom ligand that renders each to be symmetrical with respect 30 to the A' bridging group but different with respect to each other that controls the approach of each successive monomer unit that is added to the polymer chain. The steric difference between the Cp ring and the heteroatom ligand acts to block the approaching monomer from a random approach such that the monomer is added to the polymer chain in the syndiotactic configuration.

Preferable metallocene precursors for the production of syndiotactic polymers are those where S and S' are chosen such that the steric difference between the Cp and heteroatom ligand is maximized.

The chiral and non-chiral bridged metallocene precursors for the formation of the ionic catalysts of this invention may be prepared by methods known in the art. The synthesis process generally comprises the steps of 1) preparing the ligand, 2) deprotonating the acidic protons of the ligand (using BuLi, KH or other strong bases), 3) reacting the deprotonated ligand with the halide of the transition metal, 4) purifying the metallocene halide complex, and 5) reacting the metallocene dihalide with MeLi or a hydride source to give the final product.

In general, preferred mono(cyclopentadienyl) Group 4 metal compounds for the production of poly- α -olefins with enhanced tacticity are bridged species where $y=1$ as in formula 3. A method of preparing these compounds is by reacting a cyclopentadienyl lithium compound with a dihalo compound whereupon a lithium halide salt is liberated and a monohalo substituent is covalently bound to the cyclopentadiene. The substituted cyclopentadiene is then reacted with a lithium salt of the heteroatom (for the sake of illustration, a lithium amide) whereupon the halide is eliminated from the monohalo substituent group, forming thereby a lithium halide salt with the heteroatom group, preferably an amide, covalently bonded to the substituent of the cyclopentadienyl reaction product. The resulting cyclopentadienyl derivative is then reacted with a base, preferably an alkyl lithium, to remove the labile hydrogen atoms on the heteroatom and on the cyclopentadienyl ring. The cyclopentadienyl dianion is reacted with a Group 4 metal compound, preferably a tetrahalide. This general procedure yields the dichloro derivative of a bridged monocyclopentadienyl Group 4 metal complex corresponding to formula 3 ($y=1$). The dichloride complex is then converted into the appropriate hydrocarbyl derivative using a Grignard, lithium, sodium, or potassium salt of the hydrocarbyl ligand. The procedure is analogous to that used to derivatize known bis(cyclopentadienyl) complexes according to EPA 277,004.

Preferred heteroatom groups (JS') are amides such as t-butyamide, cyclododecylamide, and mesityl amide.

Preferred complexes of this type are those in which the bridging (A') group is a dialkyl, diaryl, or alkylaryl silylene or methylene, 1,1-ethylene, or

- 12 -

2,2-propylene. Most preferred bridging groups are dimethylsilylene, diethylsilylene, diphenylsilylene, and methylphenylsilylene.

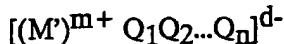
Unbridged species ($y=0$) can be prepared from a monocyclopentadienyl Group 4 trihalide complex and the lithium salt of a heteroatom moiety (amide, alkoxide, aryloxide, etc.). Suitable Group 4 metal compounds illustrative of these unbridged species include (pentamethylcyclopentadienyl) (di-t-butylphosphido) hafnium dimethyl, (pentamethylcyclopentadienyl) bis(trimethylsilyl amido) hafnium dimethyl, and (pentamethylcyclopentadienyl) (t-butoxy) titanium dimethyl.

A subclass of monocyclopentadienyl complexes, those with fluorenyl groups, have been found to produce syndiotactic polypropylene when used in accord with this invention.

Lewis acids such as, but not limited to, trialkylaluminums may be added to the catalyst system to modify the stereospecificity of the catalyst. The Lewis acid may also be tethered to the transition-metal component of the catalyst through the substituent group on the heteroatom ligand, thus adding chirality to the catalyst system. In cases where sufficiently strong Lewis acids are used, the cyclopentadienyl ligand may not require substituent groups in order to produce poly- α -olefins or polymers with blocks of isotacticity.

B. The Activator Component

Compounds useful as an activator component in the preparation of the ionic catalyst systems used in the process of this invention comprise a cation, which is a Bronsted acid capable of reacting with a ligand of the metallocene or first component, and a compatible non-coordinating anion represented by the formula:



wherein:

M' is a metal or metalloid selected from Groups V-B, VI-B, VII-B, VIII, I-B, II-B, II-A, IV-A, and V-A of the Periodic Table of Elements;

Q_1 to Q_n are selected, independently, from the group consisting of hydride radicals, dialkylamido radicals, alkoxide and aryloxide radicals, hydrocarbyl and substituted-hydrocarbyl

- 13 -

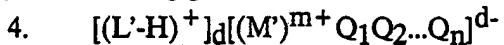
radicals and organometalloid radicals and halide, but not more than one of Q_1 to Q_n may be a halide;
m is an integer from 1 to 7;
n is an integer from 2 to 8; and
n-m=d.

5

The anion is relatively large (bulky), capable of stabilizing the active catalyst species (the Group 4 cation) which is formed when the two compounds are combined and said anion is sufficiently labile to be displaced by olefinic diolfinic and acetylenically unsaturated substrates or other neutral Lewis 10 bases such as ethers, nitriles and the like. Two classes of compatible non-coordinating anions have been described in EPA 277,003, EPA 277,004, and U.S. 5,153,157: 1) anionic coordination complexes comprising a plurality of lipophilic radicals covalently coordinated to and shielding a central charge-bearing metal or metalloid core, and 2) anions comprising a plurality of 15 boron atoms such as carboranes, metallacarboranes and boranes.

10

In general, the activator compounds containing single anionic coordination complexes which are useful in this invention may be represented by the following general formula:



20

wherein:

H is a hydrocarbon atom;

[L'-H] is a Bronsted acid

M' is a metal or metalloid;

25

Q_1 to Q_n are, independently, hydride radicals, hydrocarbyl and substituted-hydrocarbyl radicals, halocarbyl and substituted-halocarbyl radicals and hydrocarbyl- and halocarbyl-substituted organometalloid radicals, disubstituted pnictogen radicals, substituted chalcogen radical and any one, but not more than one, of Q_1 to Q_n may be halogen radical;

m is an integer representing the valence charge of M'; and

30

n is the total number of ligands Q.

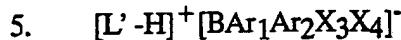
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As indicated above, any metal or metalloid capable of forming an anionic complex which is stable in water may be used or contained in the anion of the second compound. Suitable metals, then include, but are not limited to, aluminum, gold, platinum and the like. Suitable metalloids include, but are not limited to, boron, phosphorus, silicon and the like. Compounds containing anions which comprise coordination complexes

- 14 -

containing a single metal or metalloid atom are, of course, well known and many, particularly such compounds containing a single boron atom in the anion portion, are available commercially. In light of this, salts containing anions comprising a coordination complex containing a single boron atom
5 are preferred.

The preferred activator compounds comprising boron may be represented by the following general formula:



wherein:

10 B is boron is a valence state of 3;

Ar₁ and Ar₂ are the same or different aromatic or substituted-aromatic hydrocarbon radicals containing from about 6 to about 20 carbon atoms and may be linked to each other through a stable bridging group; and

15 X₃ and X₄ are, independently, hydride radicals, hydrocarbyl and substituted-hydrocarbyl radicals, halocarbyl and substituted-halocarbyl radicals, hydrocarbyl- and halocarbyl-substituted organometalloid radicals, disubstituted pnictogen radicals, substituted chalcogen radicals and halide radicals such that X₃ and X₄ will not be halide at the same time.

In general, Ar₁ and Ar₂ may, independently, be any aromatic or
20 substituted-aromatic hydrocarbon radical. Suitable aromatic radicals include, but are not limited to, phenyl, naphthyl and anthracenyl radicals. Suitable substituents on the substituted-aromatic hydrocarbon radicals, include, but are not necessarily limited to, hydrocarbyl radicals, organometalloid radicals, alkoxy and aryloxy radicals, alkylamido radicals,
25 fluorocarbyl and fluorohydrocarbyl radicals and the like such as those useful as X₃ and X₄. The substituent may be ortho, meta or para, relative to the carbon atoms bonded to the boron atom. When either or both X₃ and X₄ are a hydrocarbyl radical, each may be the same or a different aromatic or substituted-aromatic radical as are Ar₁ and Ar₂, or the same may be a straight or branched alkyl, alkenyl or alkynyl radical, a cyclic hydrocarbon radical or an alkyl-substituted cyclic hydrocarbon radical. X₃ and X₄ may also, independently be alkoxy or dialkylamido radicals wherein the alkyl portion of said alkoxy and dialkylamido radicals, hydrocarbyl radicals and organometalloid radicals and the like. As indicated above, Ar₁ and Ar₂
30 could be linked to either X₃ and X₄. Finally, X₃ and X₄ may also be linked to each other through a suitable bridging group.

- 15 -

Illustrative, but not limiting, examples of boron and other metal and metalloid compounds which may be used as an activator component in the preparation of the improved catalyst of this invention are described in EPA 277,004. The list regarding suitable activators as described in EPA 277,004 is 5 not intended to be exhaustive and other useful boron compounds as well as useful compounds containing other metals or metalloids would be readily apparent to those skilled in the art from the foregoing general equations.

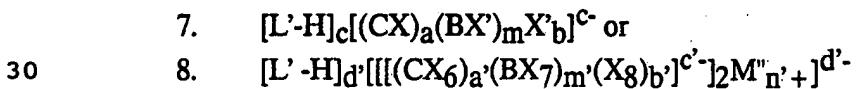
The most preferred activator compounds comprising boron may be represented by the following formula:



wherein:

F is flourine, C is carbon and B, L', and Q are defined above. Illustrative but not limiting, examples of most preferred activator compounds comprising boron which may be used in the preparation of the improved 15 catalysts of this invention include N,N-dialkylanilinium salts (L' = N,N-dialkylaniline) where Q is a simple hydrocarbyl such as methyl, butyl, cyclohexyl, or phenyl or where Q is a polymeric hydrocarbyl of indefinient chain length such as polystyrene, polyisoprene, or poly-paramethylstyrene. Polymeric Q substituents on the most preferred anion offer the advantage of 20 providing a highly soluble ion-exchange activator component and final ionic catalyst. Soluble catalysts and/or precursors are often preferred over insoluble waxes, oils, phases, or solids because they can be diluted to a desired concentration and can be transferred easily using simple equipment in commercial processes.

25 Activator components based on anions which contain a plurality of boron atoms, as described in EPA 277,003, may be represented by the following general formulae:



wherein:

[L' · H] is either H^+ or a Bronsted acid derived from the protonation of a neutral Lewis base;

35 X, X', X'', X₆, X₇ and X₈ are, independently, hydride radicals, halide radicals, hydrocarbyl radicals, substituted-hydrocarbyl radicals, halocarbyl

- 16 -

radicals, substituted-halocarbyl radicals, or hydrocarbyl- or halocarbyl substituted organometalloid radicals;

M" is a transition metal;

5 a and b are integers ≥ 0 ; c is an integer ≥ 1 ; a + b + c = an even-numbered integer from 2 to about 8; and m is an integer ranging from 5 to about 22;

b' and b' are the same or a different integer 0; c' is an integer ≥ 2 ; a' + b' + c' = an even numbered integer from 4 to about 8; m' is an integer from 6 to about 12; n' is an integer such that $2c' - n' = d'$; and d' is an integer ≥ 1 .

10 Preferred anions of this invention comprising a plurality of boron atoms comprise:

(1) A trisubstituted ammonium salt of a borane or carborane anion satisfying the general formula:

15 9. $[(CH)_{ax}(BH)_{bx}]^{cx-}$

wherein:

ax is either 0 or 1; cx is either 1 or 2; ax + cx = 2; and bx is an integer ranging from about 10 to 12;

20 (2) A trisubstituted ammonium salt of a borane or carborane or a neutral borane or carborane compound satisfying the general formula:

10. $[(CH)_{ay}(BH)_{my}(H)_{by}]^{cy-}$

25 wherein:

ay is an integer from 0 to 2; by in an integer from 0 to 3; cy is an integer from 0 to 3; ay + by + cy = 4; and my is an integer from about 9 to about 18; or

30 (3) A trisubstituted ammonium salt of a metallaborane or metallacarborane anion satisfying the following general formula:

11. $[[[(CH)_{az}(BH)_{mz}(H)_{bz}]^{cz-}]_2M^{niz+}]^{dz-}$

wherein:

az is an integer from 0 to 2; bz is an integer from 0 to 2; cz is either 2 or 3; mz is an integer from about 9 to 11; az + bz + cz = 4; and nz and dz are, respectively, 2 and 2 or 3 and 1.

Illustrative, but not limiting, examples of second components which 5 can be used in preparing catalyst systems utilized in the process of this invention wherein the anion of the second component contains a plurality of boron atoms (as in formulae 4-11) are mono-, di-, trialkylammonium and phosphonium and dialkylarylammonium and -phosphonium salts as described in EPA 277,003. List of representative phosphonium compounds 10 can be recited as illustrative second compounds, but it is simply noted that the phosphonium and substituted-phosphonium salts corresponding to the noted ammonium and substituted-ammonium salts found in EPA 277,003 may also be used as second compounds in the present invention.

15 Choice of Metallocene-Activator Pairs

In general, and while most metallocene components identified above may be combined with most activator components above to produce an active olefin polymerization catalyst, it is important for continuity of the polymerization operations that either the metal cation initially formed from 20 the metallocene component or a decomposition product thereof be a relatively stable catalyst. It is also important that the anion of the activator compound be chemically stable and bulky. Further, when the cation of the activator component is a Bronsted acid it is important that the reactivity (i.e., acidity) of the activator component be sufficient, relative to the metallocene 25 component, to facilitate the needed charge (e.g., proton) transfer. In general, metallocenes in which the non-cyclopentadienyl and non heteroatom ligands can be hydrolyzed by aqueous solutions can be considered suitable metallocenes for forming the catalysts described herein, because water (the reference Bronsted acid) is a weaker acid than the ammonium ions used as 30 the cation component in the preferred ion-exchange reagents. This concept allows one of ordinary skill in the art to choose useful metallocene components because stability to water is a basic chemical property easily determined experimentally or by using the chemical literature.

As indicated, the ionic catalyst compositions used by the process of 35 the present invention will, preferably, be prepared in a suitable solvent or diluent. Suitable solvents or diluents include any of the solvents known in

the art to be useful as solvents in the polymerization of olefins, diolefins and acetylenically unsaturated monomers. Suitable solvents, then, include but are not necessarily limited to, straight and branched-chain hydrocarbons such as isobutane, butane, pentane, hexane, heptane, octane and the like; cyclic 5 and alicyclic hydrocarbons such as cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane and the like and aromatic and alkyl-substituted aromatic compounds such as benzene, toluene, xylene, and the like. Suitable solvents also include liquid olefins which may act as monomers or comonomers including propylene, 1-butene, 1-hexene, 3-methyl-1-pentene, 4-methyl-1-pentene, 1,4-hexadiene, 1-octene, 1-decene and the like. 10 Suitable solvents further include basic solvents which are not generally useful as polymerization solvents when conventional Ziegler-Natta type polymerization catalysts are used such as chlorobenzene.

As before discussed, the active catalyst species of the ionic catalyst 15 systems used by the process of this invention is relatively stable and is not subject to the ion equilibrium deactivation as are alumoxane cocatalyzed metallocene catalyst systems. Unlike metallocene-alumoxane catalyst systems wherein, to obtain a practical level of catalyst productivity it is generally required to use an amount of alumoxane, measured as aluminum 20 atom, to provide a ratio of Al:transition metal well in excess of 1000:1; the ionic catalyst systems used in the process of this invention which are highly productive may be prepared at ratios of metallocene to activator of 10:1 to about 1:1, preferably about 3:1 to 1:1.

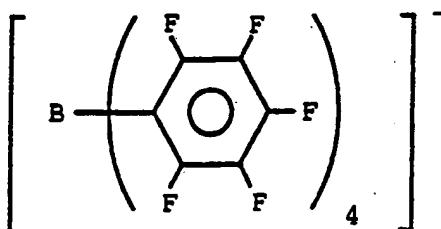
The structures of catalyst species depend on such factors as (1) the 25 metallocene used and the degree to which the cyclopentadienyl ligand of such metallocenes are substituted; (2) the nature of the anion moiety compound and the degree and type of substitution on such anions; (3) the nature of the cation moiety of the second compound, particularly in the case where the counter ion is a proton donor, the molecular size of neutral Lewis 30 base which is liberated from such cation upon loss therefrom of a proton; and (4) the ratios at which the metallocene and activator compound are employed.

With respect to the combination of the metallocene component with the activator component to form a catalyst of this invention, it should be 35 noted that the two compounds combined for preparation of the active catalyst must be selected so as to avoid transfer of a fragment of the anion,

particularly an aryl group, to the metallocene metal cation, thereby forming a catalytically inactive species. When anions consisting of hydrocarbyl anions are used, there are several means of preventing anion degradation and formation of inactive species. One method is to carry out the protonolysis 5 process in the presence of small Lewis bases such as tetrahydrofuran. Discrete complexes can be isolated from these reactions, but the Lewis base is insufficiently labile to be displaced readily by α -olefin monomers, resulting in, at best, catalysts of very low activity.

Another method of avoiding deleterious anion degradation is by steric 10 hindrance. Anions of the second component which contain aryl groups can be made more resistant to degradation by introducing substituents in the ortho positions of the phenyl rings. While active metallocene polymerization catalysts can be generated by this method, the complex reaction chemistry often prevents characterization of the catalytically active species. Steric 15 hindrance can also result from substitutions on the cyclopentadienyl ring of the metallocene component. Hence, the high degree of substitution on the cyclopentadienyl ring creates sufficient bulkiness that not only cannot the Lewis base generated by the protonolysis reaction coordinate to the metal but also polyarylborate anions without substituents on the aryl rings do not 20 transfer aryl fragments to generate catalytically inactive species.

A third means of rendering the anion of the activator compound more 25 resistant to degradation is afforded by fluorine substitution, especially perfluoro substitution, in the anion thereof. One class of suitable non-coordinating anions can be represented by the formula $[B(C_6F_5)_3Q]^-$ where Q is a monoanionic non-bridging radical as described above. The preferred anion of the activator compound of this invention, tetra(pentafluorophenyl)boron, hereafter referred to for convenience by the notation $[B(C_6F_5)_4]^-$ ($[B(pfp)_4]^-$) is virtually impervious to degradation and can be used with a much wider range of metallocene cations, including those 30 without substitution on the cyclopentadienyl rings, than anions comprising hydrocarbyl radicals. The tetra(pentafluorophenyl)boron anion is illustrated below:



- 20 -

Since the anion has little or no ability to coordinate to the metallocene cation and is not degraded by the metallocene cation, structures of the ion-pair metallocene catalyst using the $[B(pfp)_4]$ - anion depend on steric hindrance of substituents on the cyclopentadienyl ring of metallocene, 5 the nature of the cation of the activator component, the Lewis base liberated from the protonolysis reaction, and the ratio at which the metallocene and activator component are combined.

When the non-coordinating anion contains a plurality of boron atoms as described in general formulae 7 and 8, more effective catalysts are 10 obtained with activator compounds containing larger anions, such as those encompassed by general formula 8 and those having larger m values in general formula 7. In these cases it is further preferable when using second compounds which are encompassed by general formula 7, that $a + b + c = 2$. Second compounds in which $a + b + c =$ even-numbered integers of 4 or 15 more have acidic B-H-B moieties which can react further with the metallocene metal cation formed, leading to catalytically inactive compounds.

Having described the importance of choosing stable non-coordinating anions (catalyst lifetime and stability) and the science necessary to choose 20 from the list of possible options it should be noted that the structure of the stable non-coordinating anion has an effect on the polymerization properties of a particular catalyst cation. It has been discovered that even simple changes to the structure of the non-coordinating anion can lead to significant and surprising changes in the polymerization properties of the catalytically 25 active metallocene cation.

These trends are representative of typical anion effects for other metallocene polymerization catalyst systems. This property adds a new level of control over catalyst properties which does not rely on modification to the metallocene ligand system and which can be used to change molecular 30 weight, end groups, control composition distribution, and broaden the molecular weight distribution of a targeted polymer product.

Process of Polymerization

In accordance with a preferred procedure the selected ionic catalyst 35 system for controlled tacticity polyolefin production may be used to produce such poly- α -olefin by slurry polymerization using the olefin monomer as the

polymerization diluent in which the selected catalyst is dissolved in an amount sufficient to yield the type of polymer desired. Generally the polymerization process is carried out with a pressure of from about 10 to about 1000 psi (68.9 KPa - 6890 KPa), most preferably from about 40 to 600 psi (276 KPa - 4134 KPa). The polymerization diluent is maintained at a temperature of from about -10° C to about 150° C, preferably from about 20° C to about 100° C, and most preferably from about 30° C to about 90° C. The catalyst systems used by the process of this invention may also be employed in a high temperature/pressure polymerization process. In such, the pressure can be in the range of 5,000-40,000 psi and the temperature in the range of 120-300° C.

The polymerization may be carried out as a batchwise slurry polymerization or as a continuous process slurry polymerization. The procedure of continuous process slurry polymerization is preferred, in which event α -olefin and catalyst are continuously supplied to the reaction zone in amounts equal to the α -olefin and catalyst removed from the reaction zone with the polymer in the product stream. The catalyst system described herein may optionally be placed on a support medium and employed in such polymerization processes as gas phase polymerization. Additionally, scavenging agents may be employed during polymerization of olefins.

EXAMPLES

The following examples are intended to illustrate but not limit the invention. Those of skill in the art may discover other methods, not explicitly described, but within the scope of this disclosure.

A. Preparation of $B(C_6F_5)_3Q$ - Activators

In general anionic complexes of the form $[B(pfp)_3Q]^-$ can be prepared by the addition of the lithium or Grignard reagents $Li[Q]$ or $MgBr[Q]$ to $B(pfp)_3$ in ether from which reaction $Li[B(pfp)_3Q]^-$ is isolated in high yield as an etherate. The lithium salt can be converted into the final ammonium salt by treatment with $R_3NH^+Cl^-$ in methylene chloride. The insoluble lithium chloride is removed by filtration and the excess ammonium chloride is removed by washing the methylene chloride solution with water. The methylene chloride solution is dried using Na_2SO_4 , filtered and

concentrated to the point of crystallization. Addition of a counter solvent such as pentene can be used to precipitate $[R_3NH][B(pfp)_3Q]$.

The two examples below show how "living" anionically polymerized macromers can be used to prepare soluble polymer modified boron anions.

5 This reaction is general for all living anionic polymerization systems.

Example 1

In this example, $[PhMe_2NH][B(pfp)_3(PS)]$ (where PS = linear polystyrene) was prepared by the reaction of one equivalent of $B(pfp)_3$ (2.3 10 grams, 4.46 mmole) with living polystyrene macromer (prepared in toluene (20 ml) from the reaction of 10 equivalents of styrene with one equivalent of sec-butyllithium in toluene at room temperature). The reaction caused an immediate change in color from red (the color of the living macromer) to clear. The toluene was removed in vacuo and the resulting glassy solid was extracted with methylene chloride (50 ml) and treated with $[PhMe_2NH][Cl]$. 15 The lithium chloride was removed by filtration, and the resulting methylene chloride solution was washed with water (3 times using 50 ml), dried over Na_2SO_4 , filtered and evaporated to dryness. The resulting glassy solid (6.5 grams) was characterized by carbon and proton NMR.

20

Example 2

In this example $[PhMe_2NH][B(pfp)_3(PMS)]$ was prepared using the procedure described in Example 1 using 5 grams of poly(paramethylstyrene) in place of styrene.

25

B. Preparation of mono-cyclopentadienyl Metallocene Complexes

All procedures were performed under an inert atmosphere of helium or nitrogen. Solvent choices were often optional, for example, in most cases 30 either pentane or 30-60 petroleum ether could be interchanged. The choice between tetrahydrofuran (THF) and diethyl ether is a bit more restricted, but in several reactions, either could be used. The lithiated amides were prepared from the corresponding amines and either n-BuLi or MeLi. Published methods for preparing $LiHC_5Me_4$ include C.M. Fendrick et al, 35 Organometallics 1984, 3, 819 and F. H. Kohler and K. H. Doll, Z. Naturforsch, 1982, 376 144. Other lithiated substituted cyclopentadienyl

compounds are typically prepared from the corresponding cyclopentadienyl ligand and n-BuLi or MeLi, or by reaction of MeLi with the proper fulvene. TiCl₄ was typically used in its etherate form. The etherate can be prepared by simply adding TiCl₄ to ether and filtering off the solid product which is 5 then vacuum dried. TiCl₄, ZrCl₄, HfCl₄, amines, silanes, substituted and unsubstituted cyclopentadienyl compounds or precursors, and lithium reagents were purchased from Aldrich Chemical Company, Cerac or Petrarch Systems. Methylalumoxane was supplied by either Schering or Ethyl Corporation.

10 The initial preparative route chosen typically involved the isolation of intermediate products. Ease of preparation and a significant increase in yield could be obtained if one limits the number of isolated intermediates, however, when making new compounds, intermediates were commonly isolated to verify formation and to control stoichiometry in subsequent steps. 15 When intermediate products were not isolated, samples were taken and characterized by ¹H NMR prior to proceeding to the next step of the reaction.

Example 3

20 Preparation of Li₂[Me₂Si(C₁₃H₉)(N-t-Bu)]·Et₂O.

Part 1. Me₂SiCl₂ (150 ml, 1.24 mol) was diluted with ~200 ml of ether. Li(C₁₃H₉)·Et₂O (lithiated fluorene etherate, 28.2 g, 0.11 mol) was slowly added. The reaction was allowed to stir for 1 hour prior to removing the solvent via vacuum. Toluene was added and the mixture was filtered 25 through Celite to remove the LiCl. The solvent was removed from the filtrate, leaving behind the off-white solid, Me₂Si(C₁₃H₉)Cl (25.4 g, 0.096 mol).

Part 2. Me₂Si(C₁₃H₉)Cl (8.0 g, 0.031 mol) was diluted in ether. LiHN-t-Bu (2.4 g, 0.030 mol) was slowly added and the mixture was allowed 30 to stir overnight. The solvent was removed in vacuo and methylene chloride was added to precipitate the LiCl which was filtered off. The solvent was removed from the filtrate leaving behind a oily yellow liquid identified as Me₂Si(C₁₃H₉)(NH-t-Bu) (8.8 g, 0.028 mol).

Part 3. Me₂Si(C₁₃H₉)(NH-t-Bu) (8.8 g, 0.028 mol) was diluted with ether. MeLi (1.4 M, 41 ml, 0.057 mol) was slowly added and the reaction was allowed to stir for about two hours. The solvent was removed via vacuum

- 24 -

leaving behind an orange solid identified as $\text{Li}_2[\text{Me}_2\text{Si}(\text{C}_{13}\text{H}_8)(\text{N-t-Bu})] \cdot \text{Et}_2\text{O}$.

Example 4

5 Preparation of $\text{Me}_2\text{Si}(\text{C}_{13}\text{H}_8)(\text{N-t-Bu})\text{ZrMe}_2$.

Part 1. $\text{Li}_2[\text{Me}_2\text{Si}(\text{C}_{13}\text{H}_8)(\text{N-t-Bu})] \cdot \text{Et}_2\text{O}$ (8.6 g, 22.5 mmol) was added to cold ether. ZrCl_4 (5.25 g, 22.5 mmol) was slowly added and the reaction mixture was allowed to stir overnight. The solvent was removed via vacuum and toluene was added. The mixture was filtered through Celite to remove the LiCl . The filtrate was reduced in volume and cooled to -30°C to produce 4.9 grams of a yellow crystalline material identified as $\text{Me}_2\text{Si}(\text{C}_{13}\text{H}_8)(\text{N-t-Bu})\text{ZrCl}_2$.

Part 2. MeLi (8.8 mmol in ether) was added to a cooled (-30°C) solution of $\text{Me}_2\text{Si}(\text{C}_{13}\text{H}_8)(\text{N-t-Bu})\text{ZrCl}_2$ (2.0 g, 4.4 mmol) in ether. The mixture was warmed to room temperature and stirred for 1 hour. The solvent was removed in vacuo, and the crude product was extracted with pentane. The pentane extract was filtered through Celite, concentrated, and cooled to obtain 1.2 grams of an off white product identified as $\text{Me}_2\text{Si}(\text{C}_{13}\text{H}_8)(\text{N-t-Bu})\text{ZrMe}_2$ by NMR spectroscopy.

20

Example 5

Preparation of $\text{Me}_2\text{Si}(\text{C}_{13}\text{H}_8)(\text{N-t-Bu})\text{HfMe}_2$

Part 1. $\text{Li}_2[\text{Me}_2\text{Si}(\text{C}_{13}\text{H}_8)(\text{N-t-Bu})] \cdot \text{Et}_2\text{O}$ (2.8 g, 7.3 mmol) was dissolved in ether. HfCl_4 (2.35 g, 7.3 mmol) was slowly added and the reaction mixture was allowed to stir overnight. The solvent was removed via vacuum and toluene was added. The mixture was filtered through Celite to remove the LiCl . The filtrate was reduced in volume and petroleum ether was added. This was refrigerated to maximize precipitation prior to filtering off the pale orange solid. After filtration of the mixture, the product $\text{Me}_2\text{Si}(\text{C}_{13}\text{H}_8)(\text{N-t-Bu})\text{HfCl}_2$ (1.9 g, 3.5 mmol) was isolated.

Part 2. $\text{Me}_2\text{Si}(\text{C}_{13}\text{H}_8)(\text{N-t-Bu})\text{HfCl}_2$ was converted into $\text{Me}_2\text{Si}(\text{C}_{13}\text{H}_8)(\text{N-t-Bu})\text{HfMe}_2$ using the procedure described for Part 2 Example 2.

- 25 -

Example 6

Preparation of $\text{Me}_2\text{Si}(\text{C}_{13}\text{H}_8)(\text{N-Mes})\text{ZrMe}_2$ (where Mes = 2,4,6 trimethylphenyl = mesityl).

$\text{Me}_2\text{Si}(\text{C}_{13}\text{H}_8)(\text{N-Mes})\text{ZrMe}_2$ was prepared as in Example 2 using 5 $\text{Li}_2[\text{Me}_2\text{Si}(\text{C}_{13}\text{H}_8)(\text{N-Mes})]\cdot\text{Et}_2\text{O}$.

$\text{Li}_2[\text{Me}_2\text{Si}(\text{C}_{13}\text{H}_8)(\text{N-Mes})]\cdot\text{Et}_2\text{O}$ was prepared as in Example 1 using LiHNMes in place of LiHN-t-Bu.

Example 7

10 Preparation of $\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)\text{NC}_{12}\text{H}_{23}\text{TiMe}_2$

Part 1. $(\text{C}_5\text{Me}_4\text{H})\text{SiMe}_2\text{Cl}$ was prepared from Me_2SiCl_2 and $\text{C}_5\text{Me}_4\text{HLi}$ in ether using published methods.

15 Part 2. $(\text{C}_5\text{Me}_4\text{H})\text{SiMe}_2\text{Cl}$ (8.0 g, 0.037 mol) was slowly added to a suspension of $\text{LiHNC}_{12}\text{H}_{23}$ ($\text{C}_{12}\text{H}_{23}$) = cyclododecyl, 7.0 g, 0.037 mol, ~80 ml THF. The mixture was stirred overnight. The THF was then removed via a vacuum to a cold trap held at -196° C. Petroleum ether and toluene was added to precipitate the LiCl . The mixture was filtered through Celite. The solvent was removed from the filtrate. $\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4\text{H})(\text{NHC}_{12}\text{H}_{23})$ (11.8 g, 0.033 mol) was isolated as a pale yellow liquid.

20 Part 3. $\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4\text{H})(\text{NHC}_{12}\text{H}_{23})$ (11.9 g, 0.033 mol) was diluted with ~150 ml of ether. MeLi (1.4 M, 47 ml, 0.066 mol) was slowly added. The mixture was allowed to stir for 2 hours after the final addition of MeLi . The ether was reduced in volume prior to filtering off the product. The product, $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{NC}_{12}\text{H}_{23})]\text{Li}_2$, was washed with several 25 small portions of ether, then vacuum dried to yield 11.1 g (0.030 mol) of product.

30 Part 4. $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{NC}_{12}\text{H}_{23})]\text{Li}_2$ (3.0 g, 0.008 mol) was suspended in cold ether. $\text{TiCl}_4\cdot 2\text{Et}_2\text{O}$ (2.7 g, 0.008 mol) was slowly added and the resulting mixture was allowed to stir overnight. The ether was removed via a vacuum to a cold trap held at -196° C. Methylene chloride was added to precipitate the LiCl . The mixture was filtered through Celite. The solvent was significantly reduced in volume and petroleum ether was added to precipitate the product. This mixture was refrigerated prior to filtration in order to maximize precipitation. The yellow solid collected was recrystallized from methylene chloride and $\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{NC}_{12}\text{H}_{23})\text{TiCl}_2$ 35 was isolated (1.0 g, 2.1 mmol).

- 26 -

Part 5. $\text{Me}^2\text{Si}(\text{C}_5\text{Me}_4)(\text{NC}_{12}\text{H}_{23})\text{TiMe}_2$ was prepared by adding a stoichiometric amount of MeLi (1.4 M in ether) to $\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{NC}_{12}\text{H}_{23})\text{TiCl}_2$ suspended in ether. The white solid recrystallized from toluene and petroleum ether was isolated in a 57% yield.

5

C. Polymerization Studies.

Example 8 (Preparation of Syndiotactic Polypropylene)

10 $\text{Me}_2\text{Si}(\text{C}_{13}\text{H}_8)$ ($\text{N-t-Bu}\text{ZrMe}_2$ (0.020 g)(.020 g) and $[\text{PhMe}_2\text{NH}][\text{B}(\text{pfp})_4]$ (0.010 g) were combined in 2 mls of toluene. The resulting reaction product was transferred into a stainless steel autoclave reactor charged with 400 mls of liquid propylene at 40° C. The reactor was stirred for 30 minutes, the propylene was vented, and 2.3 grams of syndiotactic polypropylene was isolated ($M_w = 1850$, $M_w/M_n = 1.7$; DSC melting point = 113° C). The tacticity was determined by ^{13}C NMR spectroscopy; $\%r = 90$).

15

20 Example 9 (Preparation of Syndiotactic Polypropylene)
 $\text{Me}_2\text{Si}(\text{C}_{13}\text{H}_8)$ ($\text{N-t-Bu}\text{ZrMe}_2$ (0.20 g) and $[\text{PhMe}_2\text{NH}][\text{B}(\text{pfp})_4]$ (0.10 g) were combined in 2 mls of toluene. The resulting reaction product was transferred into a stainless steel autoclave reactor charged with 400 mls of liquid propylene at 10° C. The reactor was stirred for 2.5 hours, the propylene was vented, and 2.0 grams of syndiotactic polypropylene was isolated ($M_w = 2900$, $M_w/M_n = 1.50$; DSC melting point = 124° C). The tacticity was determined by ^{13}C NMR spectroscopy; $\%r = 95$).

25

30 Example 10 (Preparation of Syndiotactic Polypropylene)
 $\text{Me}_2\text{Si}(\text{C}_{13}\text{H}_8)$ ($\text{N-t-Bu}\text{ZrMe}_2$ (0.020 g) and $[\text{PhMe}_2\text{NH}][\text{B}(\text{pfp})_4]$ (0.10 g) were combined in 2 mls of toluene and 10 equivalents of AlMe_3 was added. The resulting reaction product was transferred into a stainless steel autoclave reactor charged with 400 mls of liquid propylene at 40° C. The reactor was stirred for 2.5 hours, the propylene was vented, and 93 grams of syndiotactic polypropylene was isolated ($M_w = 1800$, $M_w/M_n = 1.8$; DSC melting point = 113° C).

- 27 -

Example 11 (Preparation of Syndiotactic Polypropylene)

Me₂Si(C₁₃H₈) (N-t-Bu)HfMe₂ (0.030 g) and [PhMe₂NH][B(pfp)₄] (0.10 g) were combined in 2 mls of toluene. The resulting reaction product transferred into a stainless steel autoclave reactor charged with 400 mls of liquid propylene at 40° C. The reactor was stirred for 30 minutes, the propylene was vented, and 2.3 grams of syndiotactic polypropylene was isolated (Mw = 600K, Mw/Mn = 1.7). The tacticity was determined by ¹³C NMR spectroscopy; %r = 60).

10 Example 12 (Preparation of Syndiotactic Polypropylene)

Me₂Si(C₁₃H₈) (N-Mes)ZrMe₂ (0.070 g) and [PhMe₂NH][B(pfp)₄] (0.1170 g) were combined in 2 mls of toluene and 0.2 mls were used. The resulting reaction product was transferred into a stainless steel autoclave reactor charged with 400 mls of liquid propylene at 40° C. The reactor was stirred for 120 minutes, the propylene was vented, and 15 grams of syndiotactic polypropylene was isolated (Mw = 5500, Mw/Mn = 2.2; DSC. The tacticity was determined by ¹³C NMR spectroscopy; %r = 60).

15 Example 13 (Preparation of Atactic Polypropylene)

Me₂Si(C₅Me₄)(NC₁₂H₂₃)TiMe₂ (0.020 g) and [PhMe₂NH][B(pfp)₄] (0.002 g) were combined in 2 mls of toluene. The resulting reaction product was transferred into a stainless steel autoclave reactor charged with 400 mls of liquid propylene at 50° C. The reactor was stirred for 5 minutes, the propylene was vented, and 11 grams of high molecular weight atactic polypropylene was isolated (Mw = 839,000, Mw/Mn = 2.53).

20 Example 14 (Comparitive Example. Preparation of Isotactic Polypropylene Using Bis-tetrahydroindenyl Metallocene)

In this example, propylene was polymerized in liquid propylene by adding under a nitrogen atmosphere to a 1 L stainless-steel autoclave, previously flushed with nitrogen, 25 ml of a toluene solution containing a rac-dimethylsilyl-bis(tetrahydroindenyl) zirconium dimethyl (18 mg) and N,N-dimethylanilinium tetrakis(pentafluorophenyl)boron (4 mg). Propylene (400 ml) was added and the autoclave stirred at 40° C for 40 minutes. The autoclave was cooled and vented and the contents dried in a vacuum oven. The yield of isotactic polypropylene was 22 g. The weight-average molecular

- 28 -

weight of this polymer was 31,000 and the molecular weight distribution was 2.16. The polymer had a melting point of 143° C.

5 Example 15 (Comparitive Example. Preparation of
Isotactic Polypropylene Using Bis-tetrahydroindenyl
Metallocene)

In this example, propylene was polymerized in liquid propylene by adding under a nitrogen atmosphere to a 1 L stainless-steel autoclave, previously flushed with nitrogen, 25 ml of a toluene solution containing rac-
10 dimethylsilyl-bis(tetrahydroindenyl) zirconium dimethyl (50 mg) and N,N-dimethylanilinium tris(pentafluorophenyl) (polystyrene)boron (50 mg, as prepared above). Propylene (400 ml) was added and the autoclave stirred at 40° C for 60 minutes. The autoclave was cooled and vented and the contents dried in a vacuum oven. The yield of isotactic polypropylene was 8.0 g. The
15 weight-average molecular weight of this polymer was 7,800 and the molecular weight distribution was 2.66. The polymer had a melting point of 137° C.

20 Example 16 (Comparitive Example. Preparation of
Isotactic Polypropylene Using Bis-tetrahydroindenyl
Metallocene)

In this example, propylene was polymerized in liquid propylene by adding under a nitrogen atmosphere to a 1 L stainless-steel autoclave, previously flushed with nitrogen, 24 ml of a toluene solution containing rac-
25 dimethylsilyl-bis(tetrahydroindenyl) zirconium dimethyl (19 mg) and N,N-dimethylanilinium tris(pentafluorophenyl) (methyl)boron (6 mg). Propylene (400 ml) was added and the autoclave stirred at 40° C for 30 minutes. The autoclave was cooled and vented and the contents dried in a vacuum oven. The yield of isotactic polypropylene was 1 g. The weight-average molecular weight of this polymer was 3400 and the molecular weight distribution was 2.2.

35 Example 17 (Comparitive Example. Preparation of
Isotactic Polypropylene Using Bis-Indenyl Metallocene)

In this example, propylene was polymerized in liquid propylene by adding under a nitrogen atmosphere to a 1 L stainless-steel autoclave,

previously flushed with nitrogen, 25 ml of a toluene solution containing rac-
dimethylsilyl-bis(indenyl) hafnium dimethyl (10 mg) and N,N-
dimethylanilinium tetrakis(pentafluorophenyl)boron (5 mg). Propylene (500
ml) was added and the autoclave stirred at 40°C for 4.5 hours. The
5 autoclave was cooled and vented and the contents dried in a vacuum oven.
The yield of isotactic polypropylene was 7.8 g. The weight-average molecular
weight of this polymer was 555,000 and the molecular weight distribution was
1.86. The polymer had a melting point of 139°C. Analysis by ^{13}C NMR
spectroscopy indicated that the polymer was about 95% isotactic.

10

Example 18 (Comparitive Example. Preparation of
Isotactic Polypropylene Using Bis-tetrahydroindenyl
Metallocene)

In this example, propylenef was polymerized in liquid propylene by
15 adding under a nitrogen atmosphere to a 1 L stainless-steel autoclave,
previously flushed with nitrogen, 10 ml of a toluene solution containing rac-
dimethylsilyl-bis(tetrahydroindenyl) hafnium dimethyl (6 mg) and N, N-
dimethylanilinium tetrakis (pentaflourophenyl) boron (10 mg). Propylene
(300 ml) was added and the autoclave stirred at 60°C for 1 hour. The
20 autoclave was cooled and vented and the contents dried in a nitrogen stream.
The yield of isotactic polypropylene was 51.5 g. The weight-average
molecular weight of this polymer was 106,000 and the molecular weight
distribution was 2.59. The polymer had a melting point of 141.9°C.

25

Example 19 (Comparitive Example. Preparation of
Isotactic Polypropylene Using Bis-tetrahydroindenyl
Metallocene and Metallocarborane Anion)

In this example, propylene was polymerized in a hexane diluent by
adding under a nitrogen atmosphere to a 1 L stainless-steel autoclave,
30 previously flushed with nitrogen and containing 200 ml of dry, deoxygenated
hexane, 3 ml of a toluene solution containing rac-
dimethylsilylbis(tetrahydroindenyl) zirconium dimethyl (38 mg) and N,N-
dimethylanilinium bis(7,8-dicarbaundecaborato) cobaltate (III) (12 mg).
Propylene (200 ml) was added and the autoclave stirred at 50°C for 68
35 minutes. The autoclave was cooled and vented and the solid product (1 g)

- 30 -

isolated. The product had a weight average molecular weight of 1700 and a melting point of 111.5° C.

Example 20 (Comparitive Example. Preparation of
5 Isotactic Poly-1-butene Using Bis-Indenyl Metallocene)

In this example, 1-butene was polymerized in a hexane diluent by adding under a nitrogen atmosphere to a 1 L stainless-steel autoclave, previously flushed with nitrogen and containing 300 ml dry deoxygenated hexane, 20 ml of a toluene solution containing rac-dimethylsilyl-bis(indenyl) 10 hafnium dimethyl (30 mg) and N,N-dimethylanilinium tetrakis (pentafluorophenyl) boron (10 mg). 1-Butene (100 ml) was added and the autoclave stirred at 40° C for 1 hour. The autoclave was cooled and vented and the contents stirred with acetone. The solid product was filtered off and dried in a nitrogen stream. The yield of isotactic poly-1-butene was 67 g. 15 The weight-average molecular weight of this polymer was 76,000 and the molecular weight distribution was 2.51. The polymer had a melting point of 99.2° C and was found by ¹³C NMR to be 97.2% isotactic.

Example 21 (Comparitive Example. Preparation of
20 Syndiotactic Polypropylene Using
Cyclopentadienyl/Fluorenyl Metallocene)

In this example, propylene was polymerized in a hexane diluent by adding under a nitrogen atmosphere to a 1 L stainless-steel autoclave, previously flushed with nitrogen and containing 100 ml dry deoxygenated hexane, 2 ml of a toluene solution containing 2-cyclopentadienyl-2-fluorenyl-propane zirconium dimethyl (30 mg) and N,N-dimethylanilinium tetrakis (pentafluorophenyl) boron (30 mg). Propylene (400 ml) was added and the autoclave stirred at 50° C for 50 minutes. The autoclave was cooled and vented and the contents dried in a nitrogen stream. The yield of syndiotactic 25 polypropylene was 7 g. The number-average molecular weight of this polymer was 25,000 and the molecular weight distribution was 2. The polymer had a melting point of 122° C.

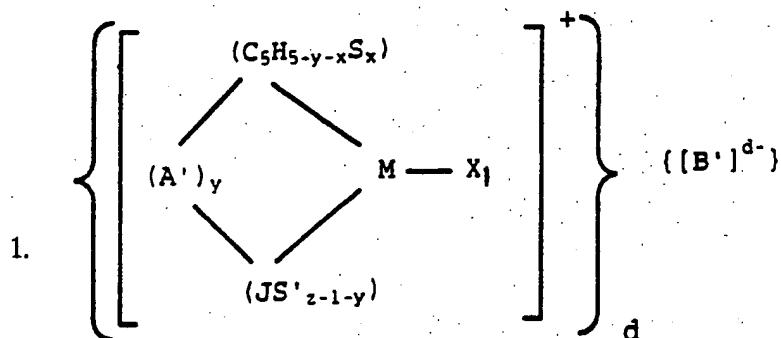
- 31 -

CLAIMS:

1. A method for producing a poly- α -olefin comprising the steps of contacting an α -olefin under polymerization conditions with an ionic catalyst complex represented by one of the following general formulae:

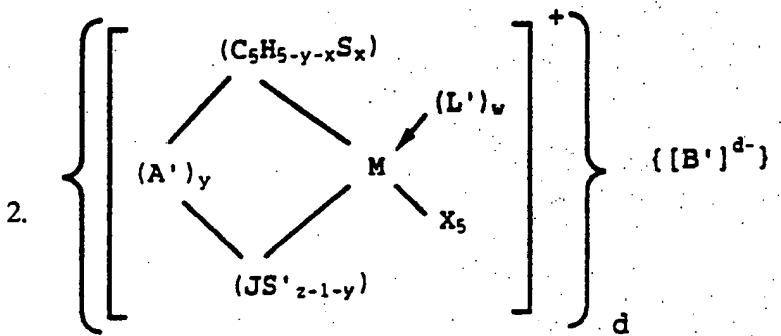
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wherein:

(C₅H₅-y-xS_x) is a cyclopentadienyl ring substituted with from zero to five S radicals;

x is from 1 to 5 denoting the degree of substitution;

M is a titanium, zirconium or hafnium;

L' is a neutral Lewis base;

A' is a bridging group, which group may serve to restrict rotation of the Cp and JS'z-1-y ligand;

X₁ is a hydride, radical, hydrocarbyl radical, substituted-hydrocarbyl radical, hydrocarbyl-substituted organometalloid radical or halocarbyl-substituted organometalloid radical;

X₅ is a hydride radical, hydrocarbyl radical or substituted-hydrocarbyl radical, halocarbyl radical or substituted halocarbyl radical, hydrocarbyl-

- 32 -

substituted organometalloid radical or halocarbyl-substituted organometalloid radical or halocarbyl-substituted organometalloid radical, which radical may optionally be covalently bonded to both M and L';

(JS'_{z-1-y}) is a heteroatom ligand in which J is an element from Group 15 of the Periodic Table of Elements with a coordination number of 3 or an element from Group 16 with a coordination number of 2; S' is a radical group which is a hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, hydrocarbyl-substituted organometalloid, or halocarbyl-substituted organometalloid; and z is the coordination number of the element J;

y is 0 or 1;

w is an integer from 0 to 3;

B' is a non-nucleophilic complex and

d is an integer representing the charge of B'.

15 2. The method of claim 1 wherein the ionic catalyst complex is prepared comprising the step of contacting

 (i) a cyclopentadienyl Group 4 metal component represented by the general formula:

20 $(C_5H_{5-y-x}S_x)$

3. (L')

25 $(A')_y$

$$\begin{array}{c}
 (C_5H_{5-y-x}S_x) \\
 \swarrow \quad \searrow \\
 (L') \longrightarrow M-X_1 \quad M-X_2 \\
 \downarrow \\
 (A')_y \\
 \swarrow \quad \searrow \\
 (JS'_{z-1-y})
 \end{array}$$

wherein:

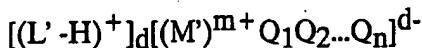
X₁ and X₂ are, independently, hydride radicals, hydrocarbyl radicals, substituted hydrocarbyl radicals, halocarbyl radicals, substituted halocarbyl radicals, and hydrocarbyl- and halocarbyl-substituted organometalloid radicals; if y=0, then w>0; and

(ii) an activator component comprising a cation capable of irreversibly reacting with a substituent of the cyclopentadienyl Group 4 metal compound to produce a cyclopentadienyl Group 4 metal cation, and an anion B'.

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- 33 -

3. The method of claim 2, wherein the activator component is represented by the following general formula:



5

wherein:

H is a hydrogen atom;

[L' · H] is a Bronsted acid;

M' is a metal or metalloid;

10 Q₁ to Q_n are selected, independently, from the group consisting of hydride radicals, hydrocarbyl and substituted-hydrocarbyl radicals, halocarbyl and substituted halocarbyl radicals and hydrocarbyl- and halocarbyl-substituted organometalloid radicals, disubstituted pnictogen radicals, substituted chalcogen radicals and any one, but not more than one, of Q₁ to 15 Q_n may be a halide radical;

m is an integer representing the formal valence charge of M'; and

n is the total number of ligands Q.

4. The method of claim 2 or 3, wherein the activator component 20 is represented by the following formula:



wherein:

25 F is fluorine, C is carbon, and Q is a hydrocarbyl or polymeric hydrocarbyl of indefinite chain length.

5. The method of claim 3 or 4, wherein Q is methyl, butyl, cyclohexyl, phenyl, polystyrene, polyisoprene, or poly(paramethylstyrene).

30

6. The method of claims 2 or 3, wherein the activator is represented by the following general formula:



- 34 -

wherein:

B is boron in a valence of state of 3+;

Ar₁ and Ar₂ are the same or different aromatic or substituted-aromatic hydrocarbyl or halocarbyl radicals and may be linked to each other
5 through a stable bridging group; and

X₃ and X₄ are, independently, hydride radicals, hydrocarbyl radicals, substituted hydrocarbyl radicals, halocarbyl radicals, substituted halocarbyl radicals, hydrocarbyl- and halocarbyl-substituted organometalloid radicals, disubstituted pnictogen radicals, substituted chalcogen radicals and halide
10 radicals, such that X₃ or X₄ are halide.

7. The method of claim 2, wherein the activator compound is represented by the general formula:

15 [L' -H]_c[(CX)_a(BX')_mX"_b]^{c-}, or
[L' -H]_d[[[(CX₆)_a'(BX₇)_m'(X₈)_b]^{c'}]₂M"_n+]^d

wherein:

C is carbon;

20 B is boron;

X, X', X", X₆, X₇ and X₈ are, independently, hydride radicals, halide radicals, hydrocarbyl radicals, substituted-hydrocarbyl radicals, halocarbyl radicals, substituted-halocarbyl radicals, or hydrocarbyl- or halocarbyl-substituted organometalloid radicals;

25 M" is a transition metal;

a and b are integers ≥ 0 ; c is an integer ≥ 1 ; a + b + c = an even-numbered integer from 2 to 8; and m is an integer ranging from 5 to 22;

20 a' and b' are the same or a different integer > 0 ; c' is an integer ≥ 2 ; a' + b' + c' = an even-numbered integer from 4 to 8; m' is an integer from 6 to 12; n' is an integer such that 2c' - n' = d; and d is an integer ≥ 1 .

8. The method of claims 2 or 7, wherein the activator component is represented by the general formula:

[L' -H]_{dz}[[[(CH)_{az}(BH)_{mz}(H)_{bz}]^{cz-}]₂M"_{nz}+]^{dz}

- 35 -

wherein:

az is an integer from 0 to 2; bz is an integer from 0 to 2; cz is either 2 or 3; mz is an integer from 9 to 11; az + bz + cz = 4; and nz and dz are, respectively, 2 and 2 or 3 and 1.

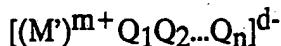
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9. The method of claims 2 or 3, wherein the activator is a trisubstituted ammonium salt of $[B(C_6F_5)_4]^-$ or $[B(C_6F_5)_3Q]^-$ wherein Q is a hydride, hydrocarbyl, substituted hydrocarbyl, halocarbyl, hydrocarbyl- or halocarbyl-substituted organometalloid, substituted pnictogen or chalogen, or 10 halide radical.

10. The method of claim 9 wherein the activator is N,N-dimethylanilinium tetrakis (pentafluorophenyl)boron.

15

11. The method of claim 1 wherein B' is represented by the formula:



wherein:

20

M' is a metal or metalloid selected from Groups V-B, VI-B, VII-B, VIII, I-B, II-B, II-A, IV-A, and V-A of the Periodic Table of Elements;

25

Q₁ to Q_n are selected, independently, from the group consisting of hydride radicals, dialkylamido radicals, alkoxide and aryloxide radicals, hydrocarbyl and substituted-hydrocarbyl radicals and organometalloid radicals and halide, but not more than one of Q₁ to Q_n may be a halide;

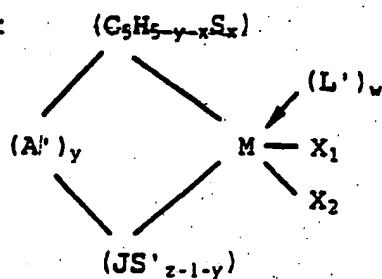
m is an integer from 1 to 7;

n is an integer from 2 to 8; and

n-m=d.

30

12. The method of claims 1 or 2, wherein the cyclopentadienyl component is of the general formula:



wherein $y = 1$ and the component contains steric differences between $(C_5H_{5-y}S_x)$ and (JS'_{z-1-y}) so as to produce a poly- α -olefin of predominantly syndiotactic stereochemical configuration.

5 13. The method of claim 12 wherein the cyclopentadienyl component contains no plane of symmetry through the metal center.

10 14. The method according to any of the preceding claims, wherein the cyclopentadienyl Group 4 metal derivative is used in a molar ratio with respect to the activator compound of from 1:1 to about 10:1 preferably from 1:1 to 3:1.

15 15. The method according to any of the preceding claims, wherein the temperature at which the polymerization is carried out is between -10° C 300° C preferably 20° C to 100° C, most preferably 30° C to 90° C.

20 16. The method according to any of the preceding claims, wherein the pressure at which the polymerization is carried out is between about 10 psi (68.9KPa) and 40,000 psi (276,000KPa), most preferably, between 40 psi(276KPa) and 600 psi (4134 KPa).

25 17. The method according to any of the preceding claims, wherein the polymers produced have a molecular weight up to 900,000 and/or less than 20,000.

18. The method according to any of the preceding claims, wherein the polymers produced have a molecular weight distribution (M_w/M_n) less than 3.

30 19. The method according to any of the preceding claims, wherein the polymers produced have terminally unsaturated units.

20. The method according to claims 12, 14, 15, 16, 17 or 18 wherein the polymer product is predominantly syndiotactic polypropylene.

- 37 -

21. The method according to claims 13, 14, 15, 16, 17 or 18 wherein the polymer product is predominantly isotactic polypropylene.

22. The method of claim 2 wherein the cyclopentadienyl component is an unbridged ($y=0$) cyclopentadienyl-heteroatom- group 4 metal compound, preferably (pentamethylcyclopentadienyl)(di-t-butylphosphido)hafniumdimethyl,

5 (pentamethylcyclopentadienyl)(bis(trimethyl-silyl)amido)hafniumdimethyl, and (pentamethylcyclopenta-dienyl)(t-butoxy)titanium dimethyl.

10 23. The method of claim 22 wherein the cyclopentadienyl component contains substituent group(s), preferably to form a fluorenyl compound.

15 24. The method of claim 1 or 2 where in the cyclopentadienyl group 4 method component is:

$\text{Me}_2\text{Si}(\text{C}_{13}\text{H}_8)(\text{N-t-Bu})\text{ZrMe}_2$;

$\text{Me}_2\text{Si}(\text{C}_{13}\text{H}_8)(\text{N-t-Bu})\text{HfMe}_2$;

$\text{Me}_2\text{Si}(\text{C}_{13}\text{H}_8)(\text{N-Mes})\text{ZrMe}_2$; or

$\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{NC}_{12}\text{H}_{23})\text{TiMe}_2$.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 93/02376

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)⁶

According to International Patent Classification (IPC) or to both National Classification and IPC
 Int.C1. 5 C08F10/00; C08F4/643

II. FIELDS SEARCHED

Minimum Documentation Searched⁷

Classification System	Classification Symbols
Int.C1. 5	C08F

Documentation Searched other than Minimum Documentation
 to the Extent that such Documents are Included in the Fields Searched⁸

III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹

Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	WO,A,9 200 333 (EXXON CHEMICALS PATENTS INC.) 9 January 1992 cited in the application see claims 1,4,6,14,16,17,21 see page 33; example 1 see example 4 see page 24, line 4 - line 5 see page 29, line 9 - line 13 ---	1-18
X	EP,A,0 418 044 (THE DOW CHEMICAL COMPANY) 20 March 1991 see claims 1-3,6,10-12 see page 6, line 4 - line 11 ---	1-6,9, 15,16
P,X	EP,A,0 495 375 (THE DOW CHEMICAL COMPANY) 22 July 1992 see claim 1 see page 4, line 32 ---	1,12 ---

¹⁰ Special categories of cited documents :¹⁰

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- ^{"O"} document referring to an oral disclosure, use, exhibition or other means
- ^{"P"} document published prior to the international filing date but later than the priority date claimed

^{"T"} later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

^{"X"} document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

^{"Y"} document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

^{"&"} document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

16 JUNE 1993

Date of Mailing of this International Search Report

13.07.93

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

FISCHER B.R.